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Detoxification of iomass hydrolysates

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Introduction

Production of transportation fuels from lignocellulosic biomass is one of the leading candidates to replace fossil-based transportation fuels [1]. Thermochemical pretreatment with dilute sulfuric acid is used to open up the biomass structure. Thermochemical pretreatment also releases compounds which are inhibitory to the microorganisms that are used in the subsequent fermentation step. Consequently the hydrolysate must be detoxified to remove inhibitory compounds.

Earlier studies [2-5] indicated the feasibility of using non-dispersive membrane extraction to remove inhibitory compounds (aliphatic acids, furan derivatives, phenolics) from biomass hydrolysates. The organic phase consisting of Alamine 336 (water insoluble tri C8-C10 alkyl amine) in octanol was pumped on one side of a polypropylene membrane while the hydrolysate was pumped on the other side. Though membrane extraction is a non-dispersive, and the solubility of octanol and Alamine 336 in the hydrolysate is very low, we have shown that octanol and Alamine 336 concentrations of 500 □g mL^{-1} and 25 □g mL^{-1} may be measured in the hydrolysate after extraction [3] which could be highly inhibitory to the microorganisms.

Practical application of membrane detoxification depends on understanding the mechanism of extraction of the toxic compounds by a tertiary amine in a slightly polar organic solvent. Here *ab initio* calculations, coupled with the implicit continuum solvation model were performed to determine the free energies associated with extraction using Gaussian 03 in order to better understand the mechanism of extraction of aliphatic acids and furan derivatives from aqueous solutions into octanol in the presence and absence of an amine extractant.

Composite membranes that contain both hydrophilic and hydrophobic surfaces will minimize transfer of the phases across the membrane due to accidental pressure fluctuations by stabilizing the liquid-liquid interface in the membrane pores [6]. A layer by layer (LbL) deposition method has been used to deposit alternating cationic and anionic polyelectrolytes on one side of a polypropylene membrane thus hydrophilizing only one side. Modified membranes were tested with real biomass hydrolysates.

Methods*Modeling* The structures of acetic acid and its cyclic dimer as well as furfural and 5-hydroxymethylfurfural (HMF) were optimized using Gaussian 03. It was not possible to model Alamine 336 directly due to the large number of atoms involved in the system. As a simplification, the structures of tertiary methyl, ethyl, propyl and butyl amines were optimized using Gaussian 03. While the relatively high solubility of these low molecular weight amines in water makes them impractical for membrane extraction, free energies for complexation were determined between various compounds in biomass hydrolysates and amines as the number of C atoms increases.

The gas phase free energies of these compounds were calculated using density functional theory (DFT) with hybrid B3LYP functional and 6-31+G(d) basis set. Their solvation free energies in water and octanol were also determined with the implicit continuum solvation model.

Experiments Flat sheet polypropylene membranes, pore size 0.45 □m were first treated with carbon dioxide plasma on one surface. Next acrylic acid vapour was introduced directly onto the membrane. After rinsing with DI water, polydiallyldimethyl ammonium chloride (PDADMAC), pH adjusted DI water rinsing, followed by polyacrylic acid (PAA) were alternatively contacted

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with the membrane to build the LbL structure. In order to verify that LbL deposition was permanent, glass chips were modified and monitored *in situ* using Fourier Transform Plasmon Resonance (FT-SPR) [7]. Membranes were characterized by measuring water contact angles. Extraction with real biomass hydrolsysates was conducted and acetic acid, furfural and HMF were measured in the hydrolysate using HPLC [2].

Results and Discussion

Table 1 summarizes the computational results. The first column gives the compound being investigated while the second and third columns give the free energy of solvation in the aqueous and organic phases. The final column gives the free energy of extraction from water to octanol. The results indicate that extraction of acetic acid in the absence of a tertiary amine is not likely while extraction of acetic acid dimers is favourable. In addition extraction of acetic acid into the organic phase in the presence of a tertiary amine is favourable. Co-extraction of water with the acetic acid dimer is also likely. Thus water may need to be removed from the organic phase during regeneration. The effects of solvent and amine hydrophobicity on extraction will be discussed.

Fig 1 gives results for modification of model glass chips. Adsorption of the alternating layers of PDADMAC and PAA was monitored by FT-SPR. Fig 1shows the position of the FT-SPR peak as a function of time during rinse and polyelectrolyte adsorption steps. Arrows indicate the time at which the solution flowing to the flow cell was changed. Relatively small changes in the peak position associated with each of the rinse steps indicates that very little polyelectrolyte is rinsed off, and the deposited layers are tightly bound. Membrane contact angels were as follows: base polypropylene, 140°; side modified by LbL deposition, 31°; side not exposed to carbon dioxide plasma, 125°. Thus one side of the membrane was successfully hydrophilized.

Fig 2 gives typical extraction results for acetic acid. In order to compare results obtained here with published data, the results are normalized by dividing by the membrane surface area and the organic phase flow rate. The results indicate that the solute flux for the base polypropylene membrane is higher than the membrane treated with acrylic acid. Interestingly, after modification with a layer of PDADMAC and PAA the flux is lower than the base membrane but higher than the acrylic acid treated membrane. These results together with furfural and HMF extraction will be discussed.

Conclusions

Ab initio calculations indicate that the presence of an amine extractant enhances extraction of carboxylic acids and furans. Base polypropylene membranes have been modified through deposition of polyelectrolytes on one side of the membrane. The resulting structure stabilizes the aqueous-organic interface in the membrane pores. Use of these modified membranes minimizes loss of either phase through the membrane.

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Solute	$\Delta G_{sol\ (water)}$ (kJ mol^{-1})	$\Delta G_{sol(octanol)}$ (kJ mol^{-1})	$\Delta G_{water\ -\ octanol)}$ (kJ mol^{-1})
Acetic acid	-32.9	-0.9	+32.0
Acetic acid dimer	-13.8	-43.6	-29.8
Acetic acid dimer/water	-69.2	-78.8	-9.6
Acetic acid dimer/2 water	-102.5	-86.2	+16.3

Acetic acid /tertiary methyl amine	-12.0	-29.3	-17.3
Acetic acid /tertiary ethylamine	-4.8	-21.3	-16.5
Acetic acid/ tertiary propyl amine	2.5	-12.6	-15.1
Acetic acid /tertiary butyl amine	2.7	-15.3	-18.3
Acetic acid dimer/tertiary methyl amine	-51.3	-60.5	-9.2
Furfural	-32.8	0.9	+33.7
Furfural /tertiary methyl amine	-115.0	-142.2	-27.2
HMF	-56.9	-4.3	+52.6
HMF /tertiary methyl amine	-5.9	-20.1	-14.2

Table 1 Solvation free energies of various compounds in water and octanol.

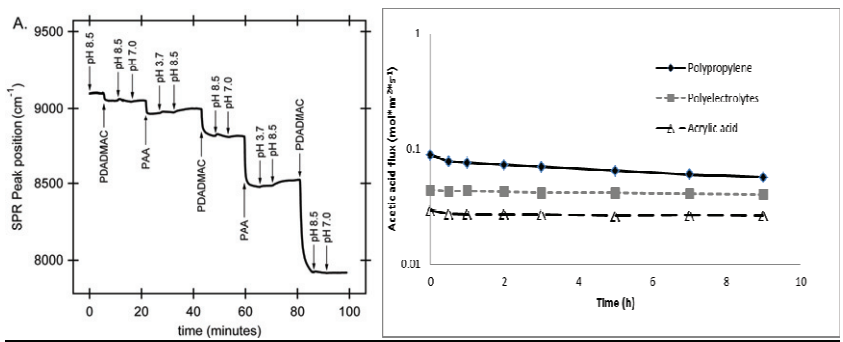

Figure 1 (left) FT-SPR peak as a function of time during the deposition on glass chips. Arrows indicate the beginning of an adsorption or rinse step. Figure 2 (right) Acetic acid flux versus time for unmodified polypropylene membrane, acrylic acid treated and after LbL deposition of PDADMAC and PAA layers.

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